

# On the low-temperature thermal properties and low-energy Fermi excitations in CeNiSn

K.A. Kikoin<sup>1</sup>, A. de Visser<sup>2</sup>, K. Bakker<sup>2</sup>, T. Takabatake<sup>3</sup>

<sup>1</sup> Kurchatov Institute, Kurchatov sq., Moscow 123182, Russia

<sup>2</sup> Van der Waals-Zeeman Laboratory, University of Amsterdam, Valckenierstraat 65/67, 1018 XE Amsterdam, The Netherlands

<sup>3</sup> Faculty of Integrated Arts and Sciences, Hiroshima University, Hiroshima 730, Japan

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**Abstract.** The thermal expansion of a single crystal of the intermetallic compound CeNiSn has been measured at low temperatures  $0.3 \text{ K} < T < 12 \text{ K}$  and in a magnetic field up to 8 T. A large anisotropy of the linear expansion is observed which is strongly influenced by the magnetic field. These data are interpreted within the theory explaining the origin of the quasigap in the heavy fermion spectrum of CeNiSn by the interplay between the heavy fermions and low-energy excitations in non-cubic Kondo lattices.

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## 1. Introduction

Recently the class of rare-earth compounds with unstable valence having the gap in the energy spectrum was extended essentially due to the discovery of several new systems with non-metallic behavior at low temperatures (see, e.g., [1]). The “conventional” semiconducting compounds SmS, SmSe, SmB<sub>6</sub>, TmTe, YbB<sub>12</sub> are based on the rare-earth elements with nearly half-filled or nearly filled 4*f*-shells. Newly found ternary compounds include Ce and U elements from the beginning of the 4*f* and 5*f* rows which usually form metallic Kondo-type or mixed valence systems. Among these systems there are compounds Ce<sub>3</sub>Bi<sub>4</sub>Pt<sub>3</sub>, U<sub>3</sub>Sb<sub>4</sub>Pt<sub>3</sub> with a well-defined and wide enough energy gap  $\Delta \sim 50\text{--}200 \text{ K}$  [2, 3], and the equiatomic compounds CeNiSn [4, 5] and CeRhSb [6] where the energy gap (or quasigap) was estimated as  $\Delta < 10 \text{ K}$ . Its existence in CeNiSn was established by studying the thermal, magnetic, transport and elastic properties. (see [7] for a review of recent experimental results).

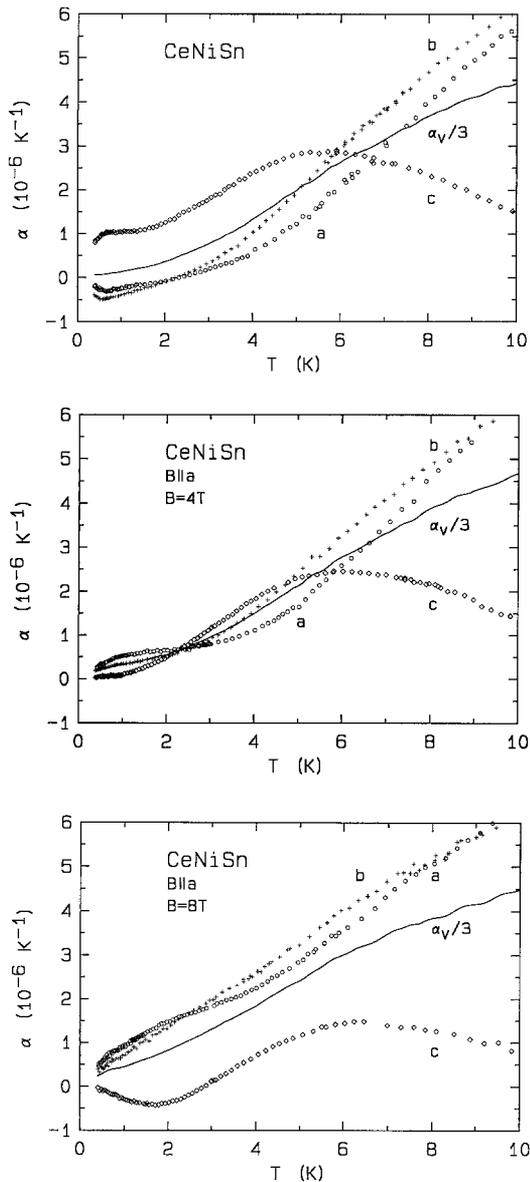
Kyogaku et al. [8] offered a phenomenological picture of the electronic spectrum containing a quasigap with the linear slopes  $\Lambda(E) \sim |E - E_F|$  and possibly a constant background density of states. This model can describe some properties of CeNiSn (the temperature dependence of the specific heat and the NMR relaxation

rate) and seems to be consistent with other anomalies in the transport and thermodynamic properties of this compound at  $T < T_0 \approx 7 \text{ K}$  ( $k_B T_0 \approx \Delta$ ). Nevertheless, the question of the origin of the low-temperature quasigap in the energy spectrum of orthorhombic Ce-based equiatomic compounds and the mechanism of its suppression in external magnetic field [9] is completely open.

In order to clarify the nature of the pseudogap in the energy spectrum of CeNiSn we study in this paper the influence of a magnetic field on the thermal expansion coefficient of this compound. The anisotropic field dependence of the low-temperature thermal properties can give essential information for the theoretical explanation of its highly unusual low-energy spectrum. Such an explanation based on the study of the crystal field effect on the spin excitations in the Kondo lattice is also offered in this paper.

## 2. Experimental

Thermal expansion measurements were performed in the temperature range  $0.3 \text{ K} < T < 12 \text{ K}$  on a single crystal-line sample prepared by the Czochralski technique. The sample was shaped by means of spark erosion into a cube with edges along the principal axes of the orthorhombic unit cell ( $a \times b \times c \simeq 2 \times 2 \times 2 \text{ mm}^3$ ). The coefficients of linear thermal expansion ( $\alpha = L^{-1} dL/dT$ ) along the different crystallographic directions,  $\alpha_a$ ,  $\alpha_b$  and  $\alpha_c$ , were measured using a sensitive parallel-plate capacitance dilatometer machined of oxygen free high-conductivity copper. The dilatometer was fixed to the cold plate of a <sup>3</sup>He-insert, which is operated with an adsorption pump. The thermal expansion was measured stepwise ( $\Delta T > 20 \text{ mK}$ ), allowing the sample to reach thermal equilibrium after each step. A RuO<sub>2</sub> chip-resistor served as thermometer. The data have been corrected for the cell-effect, i.e. the signal of the cell with a dummy copper sample. The <sup>3</sup>He-insert could be placed in a superconducting solenoid ( $B_{\text{max}} = 8 \text{ T}$ ) in order to measure the thermal expansion in constant magnetic fields. The



**Fig. 1 a-c.** Coefficients of linear thermal expansion versus temperature of CeNiSn:  $\alpha_a$  ( $\circ$ ),  $\alpha_b$  ( $+$ ) and  $\alpha_c$  ( $\diamond$ ) in a magnetic field ( $B||a$ ) of **a** 0, **b** 4 T and **c** 8 T. The solid lines indicate  $\alpha_v/3$

RuO<sub>2</sub> thermometer was calibrated in field with help of a field-insensitive capacitance thermometer.

The experimental results in zero field are shown in Fig. 1a. A large anisotropy is observed between  $\alpha_a$  and  $\alpha_b$  on the one hand and  $\alpha_c$  on the other hand. The data reveal several anomalies, but the coefficient of volume expansion,  $\alpha_v = \alpha_a + \alpha_b + \alpha_c$ , is rather structureless. No sharp anomaly appears when the gap opens (at  $\sim 7$  K [4]). A broad contribution of electronic origin appears in the high temperature part of the data. A similar observation was made for the electronic specific heat  $C(T)$  [10]. Below  $\sim 25$  K the  $C/T$  value increases monotonously up to a maximum value of  $0.18$  J/molK<sup>2</sup> at  $\sim 7$  K. This gradual increase of the  $C/T$  value is attributed to the formation of the heavy-fermion state. Below  $\sim 7$  K  $C/T$  decreases due to the opening of the gap in the fer-

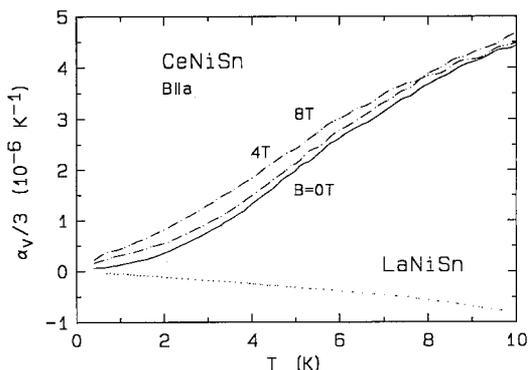
mion spectrum. Extrapolating the  $C/T$  data measured for  $T > 7$  K to  $T = 0$  K results in the enhanced  $\gamma$ -value of  $0.2$  J/molK<sup>2</sup>, and the characteristic Kondo temperature is estimated from these data as  $T^* \approx 30$  K [7].

Besides the broad high-temperature contribution, a pronounced anomaly appears below  $\sim 1.5$  K, the most clearly in  $\alpha_c$ . In  $\alpha_v(T)$  this anomaly hardly shows up. This anomaly is likely related to the stabilization of magnetic correlations. The presence of magnetic correlations below 1 K was recently put on firm footing by  $\mu$ SR experiments [11].

The magnetic properties of CeNiSn are strongly anisotropic. Electrical resistivity measurements indicate that the gap is gradually suppressed for a field of  $\approx 14$  T along the  $a$ -axis [9], while almost no effect is observed for the other directions ( $B||b$  and  $B||c$ ). Therefore we have measured  $\alpha_a$ ,  $\alpha_b$  and  $\alpha_c$  in applied magnetic fields of 4 T and 8 T. The experimental results are shown in Fig. 1b and Fig. 1c. The most striking result is the sign reversal of the coefficients of thermal expansion at low temperatures: in field  $\alpha_c(T)$  becomes positive, while  $\alpha_a$  and  $\alpha_b$  become positive. This suggests that the low-temperature magnetic correlations are strongly influenced by the magnetic field. Whether a field of 8 T is sufficient to suppress these correlations remains unclear. The field effect on the coefficient of volume expansion of CeNiSn is small but positive (see Fig. 2), yielding evidence for an enhancement of the heavy-fermion state in field.

For comparison we have also measured  $\alpha(T)$  of the non- $f$ -electron analog LaNiSn (same crystal structure as CeNiSn). The results obtained for a polycrystalline sample (after averaging the data sets along different edges of the polycrystalline cube) are shown in Fig. 2. Surprisingly,  $\alpha(T)$  of LaNiSn is negative in the investigated temperature range, indicating an anomalous phonon contribution. A large anomaly in  $\alpha(T)$  was found below  $T = 0.6$  K (not shown for the sake of clarity). This anomaly signals the transition to the superconducting state. The thermal expansion of LaNiSn is small compared to the one of CeNiSn, which evidences that  $\alpha(T)$  of CeNiSn is predominantly of electronic character.

Recently, two other data sets of the thermal expansion of CeNiSn have been reported. Uwatoko and co-



**Fig. 2.**  $\alpha_v/3$  versus temperature of CeNiSn (solid line) and LaNiSn (dotted line). The dashed-dotted lines indicate data for CeNiSn in magnetic fields of 4 T and 8 T ( $B||a$ ) as indicated

workers [12] have measured the *same* single-crystalline specimen as used in our investigation in the temperature range  $4.2\text{ K} < T < 300\text{ K}$ . The pronounced anomalies detected by these authors at  $7\text{ K}$ , when the gap opens, are not confirmed by the data in Figs. 1, 2, and therefore should be discarded. Aliev and coworkers [13, 14] investigated  $\alpha(T)$  for a polycrystalline sample ( $0.3\text{ K} < T < 10\text{ K}$ ). The pronounced negative contribution observed below  $1\text{ K}$  by these authors, is probably due to a second phase (or a non-isotropic distribution of the crystallites), as it is neither confirmed by the data on Figs. 1, 2, nor by measurements on another single-crystalline sample [15].

### 3. Effect of the weak crystal field on the low-lying excitations in the Kondo lattice

Recently, the idea of spin liquid description of strongly correlated electron systems with nearly integer valence was developed for the normal state of both high- $T_C$  cuprates [16, 17] and heavy fermion (HF) intermetallics [18–21]. Within this approach the neutral spin excitations of the Fermi-type describing the bonds between the particles rather than the particles themselves are considered as a source of the low-temperature thermodynamics. Here we use the semi-phenomenological approach formulated in [19, 20] which starts from the idea of the neutral excitation of spin origin responsible for the HF behavior of Ce-based intermetallics with the valence close to  $3+$  and considers the interaction between these fermions and other branches of the excitation spectrum. This approach was used in [22] for studying the interaction between neutral HF and crystal electric field (CEF) excitations. Referring to this paper for the details we sketch briefly in this section the main points of the theory in order to discuss the influence of a magnetic field on the low-temperature thermodynamics of CeNiSn.

According to the theory proposed in [22] the pseudo-gap in the spin-fermion spectrum appears in non-cubic Ce-based Kondo lattices provided the inequality

$$\Delta_{\text{CEF}} < T^* \quad (1)$$

is valid. Here  $\Delta_{\text{CEF}}$  is the crystal field splitting between two lowest Kramers doublets for the  $\text{Ce}(f^1)$  ion in a low-symmetry crystalline environment. This theory seems to be applicable to CeNiSn although the CEF splitting was not detected in this system whereas it was detected in the isostructural CePtSn compound [7]. Nevertheless we can refer to the nearest in chemical composition tetragonal CeNi<sub>2</sub>Sn<sub>2</sub> compound where an extremely small value of  $\Delta_{\text{CEF}} \approx 17\text{ K}$  was observed [23]. So we can hope that the crystal field produced by the Ni–Sn environment on a Ce ion in orthorhombic coordination is also weak enough, and (1) is valid for the CeNiSn system. The reasons why the CEF splitting is unobservable in CeNiSn will be presented below, and in this section we consider the consequences of (1) for the low-energy fermion excitations in this compound.

The heavy-fermion and mixed-valence systems are described usually within the Coqblin-Schrieffer modifica-

tion of the Anderson lattice Hamiltonian  $H_{\text{CS}} = H_f + H_{\text{band}} + H_{\text{hyb}}$  which can be written in the form

$$H_{\text{CS}} = \sum_{\mathbf{i}n} \sum_{\Gamma} E_{f\Gamma}^{(n)} |\mathbf{i}n\Gamma\rangle \langle \mathbf{i}n\Gamma| + \sum_{\mathbf{k}} \sum_{\gamma} \varepsilon_{\mathbf{k},\gamma} b_{\mathbf{k},\gamma}^{\dagger} b_{\mathbf{k},\Gamma} + \sum_{\mathbf{k}\mathbf{i}} \sum_{\Gamma} V_{\mathbf{k}\mathbf{i}}^{\Gamma} b_{\mathbf{k}\Gamma}^{\dagger} |\mathbf{i}, 0\rangle \langle \mathbf{i}\Gamma| + \text{H.c.} \quad (2)$$

This Hamiltonian describes the sublattice of Ce ions embedded in the Fermi sea of conduction electrons and hybridized with the corresponding partial Bloch waves. Here  $n=0, 1$  are the occupation numbers of the  $\text{Ce}(f^n)$  configurations involved in the hybridization,  $\Gamma = JM$  are the angular momentum and its projection which take the values of  $J=5/2$  and  $(-5/2 < M < 5/2)$  for the  $\text{Ce}(f^1)$  ion,  $E_{f\Gamma}^{(n)}$  is the energy level of the  $f^n$  state. The conduction band electrons are characterized by the wave number  $\mathbf{k}$  and the orbital quantum numbers  $\gamma = jm$  of the Bloch partial waves. The third term in the Hamiltonian (2) describes the hybridization between the  $f$ -electron states on site  $\mathbf{i}$  and the conduction electrons, which changes the Ce ion configuration from  $f_{\Gamma}^1$  to  $f^0$  ( $\gamma = \Gamma$  in the Coqblin-Schrieffer approximation for  $H_{\text{hyb}}$ ).

To take into account the crystal field splitting we turn from the angular momentum representation  $(\Gamma, \gamma)$  to the irreducible representation  $(A, \lambda)$  of the crystal point group. Then the multiplet  $f_{5/2}^1$  in the non-cubic CEF is split into three Kramers doublets. The CeNiSn compound crystallizes in the orthorhombic symmetry belonging to the space group  $Pn2_1a$ , but the Ce atom possesses nearly trigonal coordination: the neighboring Ni and Sn atoms form a slightly distorted hexagonal prism around the central Ce ion [24]. So we use the trigonal CEF basis  $(A, \lambda)$  in the generalized Coqblin-Schrieffer Hamiltonian and consider all interactions beyond the Coqblin-Schrieffer partial wave approximation for a trigonal lattice as a small perturbation  $H'$ ,

$$H = H_{\text{CS}}(\Gamma, \gamma \rightarrow A, \lambda) + H' \quad (3)$$

Here the states  $|A\rangle = |1\sigma\rangle, |2\sigma\rangle, |3\sigma\rangle$ , ( $\sigma = \pm$ ) are represented via  $|\Gamma\rangle$ -states as follows:

$$\begin{aligned} |1\pm\rangle &= a |\pm 1/2\rangle + b |\mp 5/2\rangle, \\ |2\pm\rangle &= |\pm 3/2\rangle, \\ |3\pm\rangle &= a |\mp 5/2\rangle - b |\pm 1/2\rangle. \end{aligned} \quad (4)$$

Then in the case of nearly integer-valent Ce ions the atomic part of the Hamiltonian can be written in the pseudofermion representation,  $|\mathbf{i}n\Gamma\rangle \langle \mathbf{i}n\Gamma| = f_{\mathbf{i}nA}^{\dagger} f_{\mathbf{i}nA}$  with the usual local constraint  $\sum_A f_{\mathbf{i}A}^{\dagger} f_{\mathbf{i}A} = 1 - \delta_{\mathbf{i}}$  where  $\delta \ll 1$

is the deviation of the valence from the integer number. It is well known that the hybridization interaction  $H_{\text{hyb}}$  with the band states close to the Fermi surface is responsible for forming the HF excitations. It was shown in [22] that the CEF excitations can influence essentially the HF spectrum provided only one of the doublets in (4), say  $|A\rangle = |\alpha\rangle$ , is involved in this hybridization and the inequality (1) is valid. Such situation can be realized in the case when only one conduction band intersects

the Fermi level. This is the case of CeNiSn according to the recent band calculations [26]. Let it be the band formed by  $p$ -electrons centered at the nearest neighbors of Ce ions. Then one can construct the linear combination of  $p$ -orbitals surrounding the  $f$ -ion and transforming according to the representation  $\alpha$ ,  $b_{i\Gamma}^+ = \sum F_{\mathbf{k}}^i b_{\mathbf{k}j}^+$ , where  $F_{\mathbf{k}}^i$  is the form factor of the  $\Gamma$  state. All other combinations of  $p$ -waves form the non-bonding orbitals and do not contribute to the low-energy hybridization. The Emery-Rice model for Cu–O plaquettes in high- $T_c$  superconductors gives an example of such a band structure.\*

Hence, we can assume according to [22] that the doublet  $|\alpha\rangle = |2\pm\rangle$  from the set (4) being hybridized with the Bloch wave  $|c\mathbf{k}\alpha\rangle$  by any of the available projection techniques (see, e.g., [18, 21]) transforms into the HF state,  $|i\alpha\rangle \rightarrow |\tilde{f}\mathbf{k}\alpha\rangle$ , and forms a band with dispersion  $\varepsilon_{\mathbf{k}\alpha}$  and the bandwidth  $\sim T^*$ . We do not specify the projection technique in our semi-phenomenological treatment because nearly all procedures available are “fragile”: the mean-field solutions are unstable against the fluctuations and violate the gauge invariance [18, 19]. But whatever procedure of introducing the spin-fermion operators is chosen, the second in energy doublet from this set, say  $|\beta\rangle = |1\pm\rangle$  can be considered as a resonance level with the energy  $E_\beta$ .\*\* This dispersionless energy level falls into the HF continuum provided the inequality (1) is valid. Now the non-CS interaction  $H'$  in the Hamiltonian (3) intermixes the states  $|\mathbf{k}\alpha\rangle$  and  $|\beta\rangle$ . The following expression was obtained in [22] for this “secondary” mixing parameter

$$g_{\mathbf{k}}^{\alpha\beta} = \frac{(\tilde{f}\mathbf{k}\alpha | V | c\mathbf{k}\alpha)(c\mathbf{k}\alpha | V' | f\mathbf{k}\beta)}{D} \quad (5)$$

where  $D$  is the width of the conduction band. The value of  $\tilde{g}_{\mathbf{k}}^{\alpha\beta}$  is strongly reduced in comparison with the bare

\* Recent experimental studies of the photoemission [25] show, first, that the valence of Ce in CeNiSn is close to 3+, and, second, that the Fermi edge has essentially Sn–5 $p$  character, maybe, with minor Ni–3 $d$  component. These results support the applicability of the model proposed in [22] to this system.

\*\* The third doublet has to be apart from the other two as follows, e.g., from the studies of the temperature behavior of the resistivity at high temperatures: the effective Kondo temperature for the sextet  $J=5/2$  as a whole is estimated as  $\approx 100$  K from these measurements [4], so can one use this value for estimating the energy interval separating this energy level and the two lower ones.

$f$ - $c$ -hybridisation because the projection procedure  $|i\alpha\rangle \rightarrow |\tilde{f}\mathbf{k}\alpha\rangle$  introduces a small parameter  $DT^*/V^2$  in the hybridization matrix elements entering the Hamiltonian (2) (see, e.g., [18, 31]). This mixing parameter can be estimated as  $\tilde{g}_{\mathbf{k}} \approx \xi T^*$  where  $\xi = \bar{V}'/\bar{V}$ . Here  $\bar{V}'$ ,  $\bar{V}$  are the values of the orthorhombic and trigonal components of the hybridization integrals between the  $f$ -electrons and their band partners in the nearest sites.

Then, including this mixing in the projection procedure by using the global constraint

$$\sum_{\mathbf{k}\sigma} [\langle f_{\mathbf{k}\alpha\sigma}^+ f_{\mathbf{k}\alpha\sigma} \rangle + \langle f_{\mathbf{k}\beta\sigma}^+ f_{\mathbf{k}\beta\sigma} \rangle] = 1 - \delta, \quad (6)$$

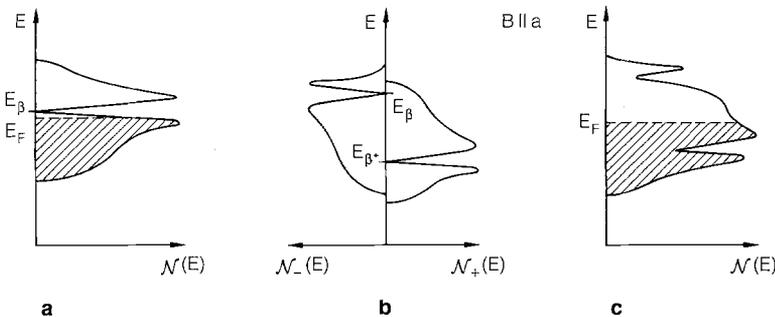
we find that the resonance  $E_\beta$  is involved into HF branch of the low-energy excitation spectrum which obtains the form

$$E_{\mathbf{k}\sigma}^{(1,2)} = \frac{1}{2} [(E_\beta + \varepsilon_{\mathbf{k}\alpha}) \pm \sqrt{(E_\beta - \varepsilon_{\mathbf{k}\alpha})^2 + 4 |g_{\mathbf{k}}^{\alpha\beta}|^2}]. \quad (7)$$

The density of states which corresponds to this spectrum is presented in Fig. 3a.

It should be noted that due to spatially non-local character of this secondary hybridization the integral  $g_{\mathbf{k}}^{\alpha\beta}$  turns into zero in some high-symmetry points of the Brillouin zone. Therefore the pseudogap  $\Delta \approx \xi T_K$  appears in the spin-fermion spectrum. The Fermi level  $E_F$  for the spin-fermions is defined by the constraint (6). It is easily seen that this level is pinned within the pseudogap provided the level  $E_\beta$  falls far enough from the upper edge of the HF band. Then the density of states  $\mathcal{N}(E)$  is highly sensitive to the difference  $\varepsilon = E - E_F$ . The form of the function  $\mathcal{N}(\varepsilon)$  depends on the type of the lattice, but one can take  $\mathcal{N}(\varepsilon) \sim \varepsilon$  for small  $\varepsilon$ .

Thus, the low-temperature thermodynamics of CeNiSn is determined by the linear slope of the density of states  $\mathcal{N}(E)$  although at  $T < 1$  K some magnetic correlations arise in the system. Such a character of Fermi excitations was found to result in the  $T^3$  dependence of the NMR relaxation rate and in the  $T^2$  term in the temperature dependence of the specific heat [8]. In our microscopic substantiation of this phenomenological treatment we imply that the fermions responsible for the low-temperature thermodynamics have mainly spin nature [19]. It is worth noting that the deficiency of spin entropy in comparison with other heavy fermion systems ( $S_{\text{magn}} \approx 0.5 R \ln 2$ ) [10] also can be ascribed to the presence of the quasigap in a spin-fermion spectrum.



**Fig. 3.** **a** The density of states  $\mathcal{N}(E)$  and the Fermi level under the constraint (6); **b** the density of states  $\mathcal{N}_\sigma(E)$  for different moment projections at  $h > h_{||}^c$ ; **c** total density of states  $\mathcal{N}(E)$  at  $B > B_{||}^c$

The inelastic neutron scattering experiments demonstrate the presence of a pseudogap in the spectrum of spin excitations in CeNiSn [27] but show no trace of the CEF excitations. It is clear from the considerations above that the theory proposed gives a natural explanation of such a transformation; the low-energy CEF levels are transformed into continuum spin excitations which are seen above the gap in a neutron scattering experiment. However, as was mentioned above, the trace of former CEF excitations is seen, at high temperature  $T > 4$ , e.g. in the logarithmic temperature behavior of the electrical resistivity  $\rho(T)$  because the contribution of the “interband” transitions  $E_{\mathbf{k}\sigma}^{(1)} \rightarrow E_{\mathbf{k}\sigma}^{(2)}$  in conduction electron scattering imitates the contribution of CEF excitations within the same energy/temperature range.

#### 4. The influence of a magnetic field on the low-temperature thermodynamics of CeNiSn

As is shown in [22] the above model explains the anisotropic suppression of the gap in an external magnetic field as observed in [9]. When the field is applied parallel to the quantization axis of the magnetic moment ( $B = B_{\parallel}$ ) the Zeeman splitting of spin fermions detunes the resonance between the Fermi level and the CEF level  $E_{\beta}$  (see Fig. 3b), so in high enough field  $B > B_{\parallel}^c$  the gap at the Fermi level disappears and conventional HF behavior is restored (Fig. 3c). The easy magnetization axis is determined by the direction of the shortest Ce–Ce distance ( $a$ -axis in CeNiSn crystal [24]). The external field applied along other crystal axes (normal to the magnetization axis) does not split the spin-fermion bands but only gives an additional contribution to the hybridization (5).

Hence, turning to the problem of the influence of a magnetic field on the low-temperature thermodynamic properties of CeNiSn we see that the maximal influence is expected in the case of the field  $B_{\parallel}a$ : Thus according to our model the conventional HF thermodynamics should be observed at  $B > B_{\parallel}^c$  due to the change of the density of states  $\mathcal{N}(E)$  illustrated by Fig. 3b. This result is in accordance with the increase of the Sommerfeld coefficient  $\gamma$  in the linear- $T$  contribution to the specific heat from the zero-field  $T \rightarrow 0$  value of 57 mJ/molK<sup>2</sup> to 125 mJ/molK<sup>2</sup> at  $B_{\parallel} = 12$  T [9].

The same mechanism is responsible for the increase of the coefficient of the thermal expansion  $\alpha(T)$  described in Sect. 2. Using the standard Maxwell thermodynamical relations one has

$$\alpha_v = \kappa \left( \frac{\partial S}{\partial V} \right)_T, \quad (8)$$

where  $\kappa$  is the compressibility. According to our approach the spin-fermion excitations give the dominant contribution to the low-temperature entropy. At present we cannot discuss the possible magnetic correlations at ultralow temperatures [11] and their contribution to the entropy and its derivatives, but we can interpret both the temperature and the field dependence of  $\alpha_v$  above

these temperatures (although still at  $T < T_{\text{CEF}}$ ), and even give the qualitative explanation of the anisotropic behavior of  $\alpha_{a,b,c}$  within this temperature interval.

Thus we write the magnetic contribution to the entropy in the form

$$S_{\text{magn}} = V \int \frac{C_{\text{magn}}(T)}{T} dT = S_u + V \left( \gamma T + \frac{\eta}{2} T^2 \right), \quad (9)$$

where  $S_u$  is the ultralow-temperature magnetic contribution to the entropy,  $V$  is the volume and  $\eta$  is the coefficient of the  $T^2$  term in the  $C(T)$  dependence [9]. Then (8) transforms to

$$\frac{\alpha_v}{\kappa} = \frac{\alpha_{ul}}{\kappa} + \gamma T \left[ 1 + \left( \frac{\partial \ln \gamma}{\partial \ln V} \right)_T \right] + \frac{\eta}{2} T^2 \left[ 1 + \left( \frac{\partial \ln \eta}{\partial \ln V} \right)_T \right], \quad (10)$$

where  $\alpha_{ul}$  is the corresponding ultralow-temperature contribution to the thermal expansion which can in principle be negative. So the spin-fermion contribution to the low-temperature entropy results in a linear + square  $T$ -dependence in zero-field behavior of the  $\alpha_v(T)$ . Indeed, it is seen from the data in Fig. 2 that the thermal expansion coefficient within the temperature interval  $1 \text{ K} < T < 5 \text{ K}$  (Fig. 2) obeys the power law  $\frac{1}{3} \alpha_v(T) = AT + FT^2$  both in zero and finite magnetic fields with the coefficient  $A$  increasing from 0.3 at  $B=0$  to 3.6 at  $B=8$  T (in units  $10^{-7} \text{ K}^{-2}$ ) and the coefficient  $F$  decreasing from 7.5 at  $B=0$  to 2.6 at  $B=8$  T (in units  $10^{-8} \text{ K}^{-3}$ ).<sup>1</sup> This result correlates with the increasing  $\gamma$  and diminishing  $\eta$  in the temperature dependence of the heat capacity in growing magnetic field [7, 9].

Both these trends can be understood within the Zeeman splitting picture for  $\mathcal{N}_{\sigma}(E)$  (see Fig. 3b, c). When the density of fermion states in zero magnetic field has the structure shown in Fig. 3a, the value of the coefficient  $A$  is determined by  $\gamma \sim \mathcal{N}(E_F)$  according to (10). The same equation gives the coefficient  $F$  which is proportional to the factor  $W$  determining the steepness of the linear slope of the v-shaped pseudogap in the density of states  $\mathcal{N}(e) = W\varepsilon$ . It is clear that  $F > 0$  at  $k_B T > E_{\beta} - E_F$ . One finds immediately that the Zeeman splitting results, in moving the Fermi level from the negative slope of  $\mathcal{N}(E)$  to a positive one, then in growing  $\mathcal{N}(E_F)$  (and  $\gamma$ ) and in making the dip in  $\mathcal{N}(E)$  more shallow, (i.e. in diminishing  $W$ ). At  $B > B_{\parallel}^c$  the linear- $T$  behavior characterizing the standard moderately HF behavior of the excitations from the Fermi surface (Fig. 3c) should restore.

Now, we should comment on the anisotropic behavior of the linear thermal expansion  $\alpha_{a,b,c}$  within the same temperature interval  $1 \text{ K} < T < 5 \text{ K}$ . It is seen from Fig. 1a, b, c that omitting the ultralow temperature anomalies the anisotropy is small enough in zero field where all three components demonstrate nearly the same behavior which do not differ from that of the bulk thermal expansion. However, in high enough fields  $B=8$  T all components change their signs: both in-plane compo-

<sup>1</sup> The linear  $\alpha(T)$  contribution of LaNiSn is not cancelled in this fitting

nents  $\alpha_{a,b}$  become positive within the whole temperature region whereas  $\alpha_c$  is negative below  $T=3$  K (Fig. 1c). Such a field dependence means on the one hand that the ultralow-temperature magnetic correlations are suppressed by the external field and on the other hand that the spin liquid in high enough magnetic field is anisotropic.

Within the framework of our model the anisotropic behavior of  $\alpha_\zeta(T)$  is governed by the values of the coefficients  $\partial \ln \gamma / \partial \ln \zeta$  and  $\partial \ln \eta / \partial \ln \zeta$  where  $\zeta = a, b, c$ , provided  $T < \Lambda$ . These derivatives depend on the lattice spacing via the values of the mixing integrals  $\bar{g}$  which are sensitive to any orthorhombic distortion as can be seen from the definition (5) of the mixing operator. Thus one should not expect strong anisotropy of the energy pseudogap (and, hence,  $\alpha_\zeta$ ) in zero magnetic field. Apparently, the only source of this anisotropy is the angular dependence of magnetic correlations which determines the term  $\alpha_{ul}$  in (10) which is beyond the scope of the present investigation.

The picture changes at higher magnetic field close to  $B_{\parallel}^*$ . In this case the pseudogap is shallow and in fact the density of states is determined rather by the value of  $T^*$  than by the hybridization with the crystal-field excitations. So the square- $T$  term in  $\alpha_\zeta(T)$  should become small and the linear term is determined mainly by the volume dependence of  $T^*$ . Taking into account the obvious relation  $N(E_F) \sim 1/T^*$  we find instead of (10)

$$\alpha \approx \kappa \gamma T \left[ 1 - \mathcal{R}(E_F) \left( \frac{\partial \ln T^*}{\partial \ln V} \right)_T \right] + \mathcal{O}(T^2). \quad (11)$$

Here  $\mathcal{R}(E_F)$  is an additional factor arising in the multi-band situation [29]. It is believed that  $-\partial \ln T^* / \partial \ln V \gg 1$  [29], so the second term is dominant in the square brackets.

Now the anisotropy of  $\alpha_\zeta$  is determined by the anisotropic derivatives  $\partial \ln T^* / \partial \ln \zeta$ . As was mentioned above, both the on-site and intersite correlations can contribute to the characteristic energy  $T^*$ . According to some recent approaches [18, 19, 21] the latter contribution can be prevailing, and in this case the difference between the in-plane components ( $\zeta = a, b$ ) and  $z$ -component ( $\zeta = c$ ) can be easily understood. If only the nearest-neighbor RKKY exchange interaction between the  $f$ -ions in zigzag chains determines the parameter  $T^*$ , then

$$\left| \frac{\partial \ln T^*}{\partial \ln a, b} \right| \gg \left| \frac{\partial \ln T^*}{\partial \ln c} \right|. \quad (12)$$

So the spin-fermion contribution to the in-plane components  $\alpha_{a,b}$  is large in comparison with that to  $\alpha_c$ . If the negative lattice contribution to  $\alpha(T)$  which was seen in LaNiSn (Fig. 2) is present also in CeNiSn, then one can explain the low-temperature negative slope in  $\alpha_c$  by the fact that the positive spin-contribution cannot overcome this trend at lowest temperatures, and only the square- $T$  contribution makes  $\alpha_c$  positive.

As was pointed out by Bastide and Lacroix [29] the pseudogap structure of the fermion density of states can result in a negative slope of the linear  $\alpha(T)$  dependence

due to the factor  $\mathcal{R}(E_F)$ , but such dependence arises only in very special case of extremely steep (nearly vertical) slope of the density of states within the pseudogap which is not seen in CeNiSn. Other possibilities of anomalous thermal expansion coefficient could be connected with specific behavior of the orthorhombic crystal field under uniaxial deformation, but at present even qualitative conclusions about CEF parameters seem to be premature.

## 5. Concluding remarks

We have investigated the influence of a magnetic field on the low-temperature thermodynamical properties of the CeNiSn compound, and found that a correlation exists for the spin entropy related properties such as the specific heat and the coefficient of thermal expansion. The theory explaining the origin of the pseudogap in the low-temperature fermion spectrum is based on the assumptions which are far from being universal for the Kondo insulators. Indeed, we think that one should not look for a single explanation of the low density of carriers in various Kondo-lattice systems, and the properties of cubic ternary compounds like  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  differ essentially from those of the orthorhombic CeNiSn and related systems. According to the theory proposed the quasigap behavior of the Kondo lattices is an extremely exotic situation which arises on the background of the ‘standard’ heavy-fermion behavior. At least three conditions are necessary for its realization: noncubic symmetry of the crystalline cell around Ce ions, a single partial wave of conduction electrons dominating on the Fermi surface and small crystal field splitting obeying (1). Some arguments are presented in the paper in favor of the applicability of this model to CeNiSn although the situation with the crystal field splitting demands additional experimental efforts.

The spin origin of the excitations with the pseudogap is multiply emphasized in this text. However, the question of existence of the corresponding gap in the charge-fermion excitations is far from being solved. In the mean-field approximations [18, 31, 30] the charge-excitation gap originates from spin-charge hybridization, but this simple picture meets theoretical objections and seems to be inconsistent with the charge transport related properties of the Ce-based heavy fermion systems [19, 20, 30]. The studies of transport properties of CeNiSn give some arguments in favor of such ‘transfer’ of the gap from spin-fermion to charge-fermion excitations. However the gap is hardly seen in the resistivity measurements. Besides, the very large, nearly temperature-independent resistivity along the  $a$  axis and the quasi logarithmic behavior of the low-temperature resistivity along the two other axes [9] yields evidence in favor of strong scattering of conduction electrons by the spin-liquid excitations. In any case the question of transport phenomena in CeNiSn and related compounds demands further theoretical investigation.

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